THE CO2 SYSTEM IN THE MEDITERRANEAN SEA: A BASIN-WIDE PRESPECTIVE

M. Álvarez [1]*, A. Luchetta [2], H. Sanleón [1], L. Mintrop [3], T. Tanhua [4] and G. Civitarese [5]
[1] Instituto Español de Oceanografía - marta.alvarez@co.ieo.es
[2] ISMAR, Trieste
[3] MARIANDA, Kiel
[4] Geomar, Kiel
[5] OGS, Trieste

Abstract
During April-May 2011 two cruises (M84/3, RV Meteor, Istambul-Vigo, and EF11, RV Urania, Bari –La Spezia) overdetermined the CO_2 system in the MedSea for the first time. The internal consistency analysis for pH, alkalinity and total inorganic carbon confirmed the use of CO2 constants from Mehrbach et al. (1973) [1] and others [2] and [3]. This analysis reveals some insights about the peculiar physico-chemical characteristics of MedSea waters. Vertical distributions of these properties will be presented and discussed along with property-property plots to characterize the different water masses in the MedSea subbasins. The sensitivity of MedSea waters to CO2 increase will be discussed using the vertical distribution of buffer factors and the saturation state for calcite and aragonite

Keywords: Chemical speciation, South-Western Mediterranean, South-Eastern Mediterranean, Tyrrhenian Sea, Ionian Sea

Introduction
The studies about CO_2 variables in the MedSea are relatively scarce [4] despite its relevance as a small laboratory for ocean processes [5] and its significant contribution to the storage of anthropogenic carbon [6]. In this study will present the first internal consistency analysis for CO_2 measurements in the MedSea although partial, using pH, alkalinity (TA) and dissolved inorganic carbon (DIC) data collected during the M84/3 and EF11 cruise, some interesting results related with the peculiarity of the MedSea waters are obtained. Additionally, basin-wide and subbasin vertical distributions of CO_2 species will be presented. The sensitivity to the CO_2 increase in the atmosphere will be studied using several buffer factors [7] and the saturation state for calcite and aragonite.

Methods
During the M84/3 (on board) and EF11 (at lab) cruises (Figure 1) pH was measured spectrophotometrically following [8], TA with potentiometric methods [9] and [10] and DIC was also measured with a S

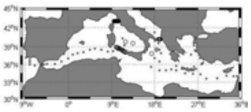

Fig. 1. Figure 1. Mediterranean Sea map with the stations sampled during the Meteor M84/3 (dots) and Urania EF11 (circles) cruises.

OMMA coulometric method. Certified reference materials were used to control the quality of our measurements.

Results and discussion
Using data from M84/3 the preferred combination of constants is the following: for CO_2 those from Merhbach et al. (1973) refitted [1], for sulphate [2] and for total borate the equation by [3]. This is also the preferred option for global synthesis studies as GLODAP or CARINA. In studying the relationship between the residuals (measured minus calculated values) for pH and TA a clear distinct relation is detected for high salinity waters in the MedSea.
Deep waters under 500 dbar in the eastern MedSea present a quite homogeneous pH25T, TA and DIC distribution, 7.966±0.004, 2614±4 umol/kg and 2310±5 umol/kg, respectively, while in the western basin are more variable 7.907±0.045, 2525±9, 2264±8, respectively. In the pressure range between 150 and 500 dbar, Levantine Intermediate water evolves in the eastern basin for pH25T, TA and DIC values from 7.982±0.02, 2626±7, 2308±13 to 7.891±0.02, 2576±13, 2319±14 in the western basin, respectively.
We studied different buffer factors [7], which quantify the sensitivity of MedSea waters CO_2, pH and carbonate saturation state to changes in DIC (at constant TA, e.g., air-sea CO_2 exchange) and TA (at constant DIC, addition of strong acid or base). We found that MedSea waters are more resistant to changes in DIC and/or TA than Atlantic waters to the west of the Strait of Gibraltar, because any buffer factor is lower in the Atlantic. The CO_2 system in the western basin is in general more sensitive to changes in DIC and/or TA than the eastern part, buffer factors are lower in the western MedSea.
The CO_2 sensitivity to changes in DIC at constant TA (air-sea CO_2 exchange) is the highest, then the change in the saturation state due to additions of a strong acid or base, then the change in the saturation state due to air-sea CO_2 exchange, then the change in pH due to the air-sea CO_2 exchange (equivalent to the change in CO_2 due to a strong acid /base addition). Finally, MedSea waters are able to buffer changes in pH due to strong acid/base additions.

References
1 - Dickson, A. G. and F. J. Millero, F.J, 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep Sea Res.*, 34: 1733–1743.
2 - Dickson, A.G., 1990. Standard potential of the reaction AgCl(s) + .5H2 (g) = Ag(s) + HCl(aq) and the standard acidity constant of the ion HSO4– in synthetic sea water from 273.15 to 318.15 K. *The Journal of Chemical Thermodynamics*, 22: 113–127.
3 - Uppstrom, L.R., 1974. The boron/chlorinity ratio of deepsea water from the Pacific Ocean. *Deep Sea Res. and Oceanographic Abstracts*, 21: 161–162.
4 - Álvarez M., 2012. The CO2 system observations in the Mediterranean Sea: past, present and future, in: CIESM, Designing Med-SHIP: a Program for repeated oceanographic surveys. *Nº43 in CIESM Workshop monographs* [F. Briand Ed.], 164 pp, Monaco.
5 - Bergamasco A. & Malanotte-Rizzoli P., 2010. The circulation of the Mediterranean Sea: a historical review of experimental investigations. *Advances in Oceanography and Limnology*, 1:1, 11-28.
6 - Schneider, A., Tanhua T., Körtzinger A., and Wallace D. W. R., 2010. High anthropogenic carbon content in the eastern Mediterranean. *J. Geophys. Res.*, 115, C12050, doi:10.1029/2010JC006171
7 - Egleston, E. S., Sabine C.L., and Morel F. M. M., 2010. Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity. *Global Biogeochem. Cycles*, 24, GB1002, doi:10.1029/2008GB003407.
8 - Clayton T. and Byrne R., 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale concentration scale calibration of m-cresol purple and at-sea results. *Deep-sea Res.* I, 40: 10, 2115-2129.
9 - Pérez, F.F. and Fraga F., 1987. A precise and rapid analytical procedure for alkalinity determination. *Mar. Chem.*, 21: 169-182
10 - Hernandez-Ayon J.M., Belli S.L., Zirino A., 1999. pH, alkalinity and total CO2 in coastal seawater by potentiometric titration with a difference derivative readout. *An. Chim. Acta* 394: 101– 108.